

COURSE MANUAL

DIRECTED ASSISTANCE MODULE NO. 5:

PROCESS CONTROL FOR SYSTEMS USING CHLORAMINES

Date Created: May 15, 2007

Date(s) Revised: August 13, 2007 *(To correct an error on page 16)*

October 8, 2007 *(To include a cover page, incorporate a course description and agenda, and add chapter headings)*

May 14, 2008 *(To correct an error in on page 7 of the Course Description)*

September 29, 2010 *(To correct an error in on page 2)*

COURSE DESCRIPTION

DIRECTED ASSISTANCE MODULE NO. 5:

PROCESS CONTROL FOR SYSTEMS USING CHLORAMINES

- A. Course Objectives:** The purpose of this course is to provide a combination of classroom and hands-on training to the staff of any public water system that treats with chloramines. After receiving the training, the water system's staff should be able to:
1. explain how chloramines form and how to control operating conditions to minimize competing reactions;
 2. identify suitable points to apply chlorine and ammonia within the plant;
 3. determine the appropriate sequence that chlorine and ammonia should be at introduced each application point;
 4. estimate the amount of chlorine and ammonia to add at each application point;
 5. conduct process control tests and interpret the results; and
 6. make appropriate adjustments to chemical feed rates.
- B. Expertise Required:**
1. **Instructor:** This Directed Assistance Module must be given by an instructor who understands and can demonstrate the steps needed to establish appropriate chlorine and ammonia feed rates, is able to use the various Feed Rate and Ratio Calculator spreadsheets, and is comfortable working with computers. The instructor must be capable of completing all of the objectives of this DAM. The TCEQ would prefer that the instructor hold a Class C or higher Water Operators license.
 2. **Participant:** The public water system staff attending this course should be familiar with the disinfection process and monitoring regimen used at their water treatment plant and either already hold a Water Operators license or at least have a basic understanding of potable water chlorination.
- C. Facilities and Materials Required at the Treatment Plant:**
1. **Instructor:** The instructor must provide all of the materials described in the *Course Description and Instructor Guide for Directed Assistance Module No. 5*.
 2. **Training Site:** This training is to be conducted at a water treatment plant which is able to provide the materials and equipment shown in Table 1.

TABLE 1: MATERIALS AND EQUIPMENT REQUIRED AT THE TREATMENT PLANT

Quantity	Item
1	Monochloramine Test Kit
1	Free Ammonia Test Kit
1	Total and Free Chlorine Test Kit
1	Computer with the Microsoft Excel 2000 program (or a later version) installed
1	Material Safety and Data Sheet (MSDS) for the liquid ammonium sulfate (LAS), ammonium hydroxide (aqueous ammonia), sodium hypochlorite (liquid bleach), and calcium hypochlorite (solid bleach) used at the plant.
1	Hydrometer, if the system is using liquid ammonium sulfate (LAS), liquid ammonium hydroxide (aqueous ammonia), or liquid bleach (sodium hypochlorite solution)
1	Scale or balance, if the system is using calcium hypochlorite to make its own chlorine solution
1	A calibration cylinder on each chemical feed pump or a 100, 200, or 500 mL graduated cylinder to measure chemical feed rates
1	A separate rotameter or feed pump for each gas chlorine or ammonia application point.
	Protective clothing (safety glasses, gloves, etc) when measuring chemical feed rates.

D. Deliverables: During this training event, the plant staff and Instructor will produce the following documentation:

1. the completed Participant Sign Up Sheet
2. the completed Plant Design and Feed Rate Information Form;
3. A printout of at least one worksheet from Feed Rate and Ratio Calculator spreadsheet with data entered for at least one application point at the plant;
4. the completed Recommended Action Plan Form;
5. the completed Plant Questionnaire from each participant; and
6. the completed Project Completion Form.

E. Provisional Agenda: The completion of this Directed Assistance Module is expected to take approximately eight hours. The provisional agenda for the DAM is shown in Table 2.

TABLE 2: PROVISIONAL AGENDA FOR DAM5

Time	Activity
8:00 – 8:15	Introductions and overview (15 minutes)
8:15 – 9:00	Plant tour (45 minutes)
9:00 – 9:30	Chemistry (30 minutes)
9:30 – 10:15	Breakpoint curve (45 minutes)
10:15 – 10:30	Break (15 minutes)
10:30 – 11:30	Weight-based Dose and Feed Rate (60 minutes)
11:30 – 12:30	Lunch (60 minutes)
12:30 – 1:45	Applying the Concepts (75 minutes)
1:45 – 2:30	Sample Collection, Laboratory Analyses and Data Interpretation – Part 1 (45 minutes)
2:30 – 2:45	Break (15 minutes)
2:45 – 3:30	Sample Collection, Laboratory Analyses and Data Interpretation – Part 2 (45 minutes)
3:30 – 4:10	Chloramination Spreadsheet (40 minutes)
4:10 – 4:30	Residual Maintenance and Distribution System Monitoring (20 minutes)
4:30 – 4:50	Action Plan (20 minutes)
4:50 – 5:00	Wrap-up and questionnaire (10 minutes)

F. Description of Activities:

1. Introductions and overview (15 minutes)

The instructor will explain the purpose of the directed assistance and what needs to be accomplished before you leave.

Participants that wish to receive Continuing Education Units (CEUs) must sign the Participant Sign Up Sheet which the instructor will provide.

2. Plant tour (45 minutes)

The instructor will accompany the plant staff on a limited plant tour. During the plant tour, The instructor will document:

1. the general layout of the treatment units,
2. the capacity of the chlorine and ammonia feeders,
3. the location of all active and standby disinfectant (O_3 , ClO_2 , Cl_2 , and ammonia) feed points,
4. the location of any existing sampling taps that should be used to monitor the chloramination process, and
5. the location that the plant staff should install additional sampling taps.

During the plant tour, the instructor and participants will begin completing the Plant Information Form provided by the instructor.

3. Chapter 1: Chemistry (30 minutes)

The instructor will:

1. Discuss the chemical reactions that occur during chloramination and explain how excess chlorine or ammonia levels can affect the reaction;
2. Discuss the importance of understanding the difference between organic ammonia and inorganic (free available) ammonia.
3. Explain why free chlorine and free available ammonia cannot coexist in the same sample to any significant degree and why it is necessary to be able to measure free chlorine, total chlorine, monochloramine, and free available ammonia.
4. Discuss the relationship between molecular chemistry and weight-based chemistry.
5. Explain how we derive the theoretical values for the weight-based chlorine:ammonia and chlorine:nitrogen ratios and how operating at other ratios influences the reactions that occur.
6. Begin introducing the issue of how competing reactions and reaction conditions can influence plant design and operations.

4. Chapter 2: Breakpoint curve (45 minutes)

The instructor will:

1. Discuss the breakpoint curve in general and explain in more detail what chemical reactions are occurring at each stage of chlorination.
2. Use the breakpoint curve as a visual aid to explain various operational scenarios and to help participants understand:
 - a. the importance of maintaining the proper chlorine:ammonia ratio and
 - b. what happens if the proper ratio is not maintained.
3. Explain and emphasize why chlorine needs to be added before ammonia when treating raw water and why ammonia should be added first when boosting the monochloramine residual in treated water.
4. Continue the discussion of competing reactions and emphasize what happens in the real world when excess chlorine or ammonia is applied.
5. Continue the discussion of how the plant staff can use analytical results to evaluate the chloramination process.

5. Break (15 minutes)

6. Chapter 3: Weight-based Dose and Feed Rate (60 minutes)

The instructor will:

1. Review the relationship between flow rate, feed rate, and dose.
2. Explain how the chemical concentration of various molecular species can affect relative reaction rates.
3. Discuss the benefits of selecting an appropriate analytical method for chlorine and ammonia.
4. Explain the difference in the various reporting methods and how results can be properly interpreted even if the instrument at the lab does not offer multiple reporting options.
5. Review the concept of parts per million (ppm) on a weight-to-weight basis and how it can be used to compare dosage and analytical results.
6. Ensure that the participants understand the difference between applied chemical dose and effective reactant dose, especially at plants feeding liquid bleach and liquid ammonium sulfate.

At plants using liquid chemicals, the instructor will also:

7. Explain the importance of understanding how the vendor reports the concentration of any liquid chemical and
8. Demonstrate how to convert volumetric feed rates to a weight-based effective chemical dose for one of the liquid chemicals used at the plant.

7. Lunch (60 minutes)

8. Chapter 4: Applying the Concepts (75 minutes)

The instructor will:

1. Review the process control loop and discuss how the approach can be applied to effectively control the chloramination process.
2. Discuss the different types of data that the operator will need to obtain.
3. Address the relationships between sampling sites, laboratory testing, and goal setting to help the participants identify appropriate sampling sites and laboratory tests for each chlorine and ammonia application point at the plant.
4. Explain how operators can use the collected data to evaluate the status of the chloramination process and develop a response to unacceptable operating conditions.
5. Ensure that the plant staff understands how the data is used make appropriate feed rate adjustments and to verify the impact of each adjustment after it is made.
6. Review the 11 Steps in the manual step-by-step approach for evaluating and adjusting the chloramination process.

The participants will:

1. Work with the instructor to identify suitable chlorine and ammonia feed points and appropriate sampling sites within the plant.

9. Sample Collection, Testing, and Data Analysis – Part 1 (45 minutes)

The instructor and participants will:

1. Select an application point where there are currently upstream and downstream sample taps/sites.
(Note: If possible, utilize an application point where it will be possible to evaluate a change in operating conditions. Due to the limited amount of time available for this topic, an optimum application point would allow the plant staff to detect a change in the downstream tap within 15 minutes of a feed rate adjustment.)
2. Identify appropriate performance targets for total chlorine, free chlorine, monochloramine, and free ammonia that are applicable to the selected application point.
3. Evaluate the results and determine what adjustments should be made to the chlorine and ammonia feed rates.
4. Observe the plant staff as they make any necessary adjustments to the chlorine and ammonia feed rates.
5. Complete Part III of the Plant Information Form.

The instructor will:

1. Observe the participants as they collect a sample from two application point sample taps and the sample tap at the point of entry to the distribution system.
2. Observe the participants as they run the laboratory analysis for free chlorine, total chlorine, monochloramine, and free available ammonia.
3. Identify and correct any sampling or analytical errors observed.
4. Verify the accuracy of the participant's calculations.
5. If a feed rate change is needed, ensure that the change is made properly.

10. Break (15 minutes)

11. Sample Collection, Testing, and Data Analysis – Part 2 (45 minutes)

The instructor and participants will:

1. Assist the participants as they identify appropriate performance targets (total chlorine, free chlorine, monochloramine, and free ammonia) that are applicable to the remainder of the current application and monitoring points.
2. Complete Part IV of the Plant Information Form.

If the time allows, the instructor and participants will:

3. verify the impact on the treatment process by running another set of samples from the upstream and downstream sample taps.
4. Assist the plant staff as they interpret the second set of data and assess the impact adjustments were made to the chlorine and ammonia feed rates.

12. Chloramination Spreadsheet (40 minutes)

The instructor will:

1. Install the Chloramination Spreadsheet on one of the plant's computers. If possible, the spreadsheet will be installed on the "Desktop" of the computer nearest the laboratory or the control room.
2. Move the appropriate worksheets to the front of the spreadsheet.
3. Demonstrate how the spreadsheet can be used as a tool to help the plant staff make appropriate changes to the various chemical feed rates.

The participants will:

1. Enter data for the application point where data was collected onto one of the worksheets.
2. Use the spreadsheet to evaluate the impact of possible changes to the chlorine and ammonia feed rates.

11. Chapter 5: Residual Monitoring and Maintenance in Distribution (20 minutes)

The instructor will:

1. Discuss the general control strategies that can be used at the plant and in the distribution system to minimize nitrification.
2. Discuss the importance of notifying the TCEQ prior to doing a "free chlorine" burn.

12. Recommended Action Plan (20 minutes)

The instructor and participants will:

1. Identify specific steps that should be taken to implement an effective chloramination process at the treatment plant.
2. Document the steps using the Recommended Action Plan Form provided by the instructor.

13. Wrap-up and Questionnaire (10 minutes)

Each participant will complete the Plant Questionnaire provided by the instructor.

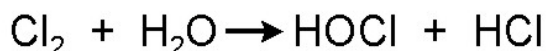
The instructor will complete the DAM Completion Form.

Before we begin discussing how to control the chloramination process, we need to review several things, including:

- The chemistry of the chloramination;
- The relationship between free ammonia, monochloramine, free chlorine, total chlorine, and combined chlorine;
- The relationship between molecular-based units of measurement and weight-based units of measurement;
- The breakpoint curve and how it relates to the chloramination process;
- The relationship between applied dose, effective dose, and feed rate . . . especially for liquid chemicals; and
- some other stuff I have probably forgotten to list.

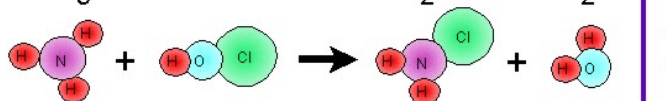
CHAPTER 1: UNDERSTANDING THE CHEMISTRY

Chlorination



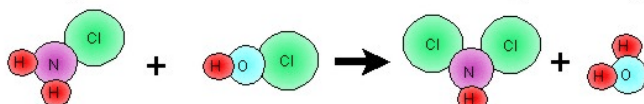
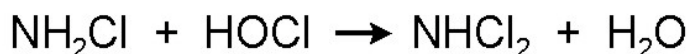
Chlorine + Water \rightarrow Hypochlorous acid + Hydrochloric acid

Chloramination

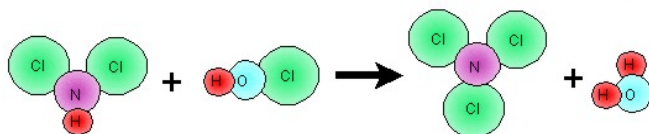
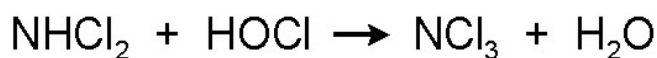


Ammonia + Hypochlorous Acid \rightarrow Monochloramine + Water

The
desired
reaction



Monochloramine + Hypochlorous Acid \rightarrow Dichloramine + Water



Dichloramine + Hypochlorous Acid \rightarrow Trichloramine + Water

These chemical equations show the molecular ratios of the different molecules or ions that are (or at least could be) present following the chloramination process. These molecular species are:

free available chlorine (FAC)	HOCl and OCl^- (hypochlorous acid and the hypochlorite ion)
free available ammonia (FAA)	NH_3
monochloramine (mono)	NH_2Cl
dichloramine (di)	NHCl_2
trichloramine (tri)	NCl_3

When we chloramine, we try to form monochloramine molecules. Monochloramine is our desired product because we know a lot about its effectiveness as a disinfectant and it produces the least offensive taste of any of the chloramine species. Although some research indicates that dichloramine and trichloramine are effective disinfectants, we try to avoid forming them because they are less stable than monochloramine and are associated with a variety taste and odor problems. Organic chloramines can also form when chlorine reacts with organic compounds that contain an ammonia (amine) group. Organic chloramines will react with DPD to give a positive result but we don't know much about how effective they are as a disinfectant. Therefore, we consider organic chloramines to be interfering substances rather than a true disinfectant.

The equations also show that one molecule of monochloramine will form when one molecule of chlorine reacts with one molecule of free available ammonia. However, if we have too much chlorine present, we run out of ammonia molecules and the excess chlorine reacts with our monochloramine molecules to form dichloramine. At really high chlorine levels, we can convert dichloramine molecules to trichloramine.

Finally, the equations show that free chlorine and free available ammonia cannot coexist to any significant degree because they will react with each other. Furthermore, it is extremely unlikely that free chlorine and monochloramine will exist in the same sample for very long since the free chlorine also reacts with monochloramine.

In this training, we are going to use the following (somewhat unconventional) terminology.

total available chlorine (TAC)	Includes free chlorine, NH_2Cl , and combined chlorine
combined chlorine	Includes NHCl_2 , NCl_3 , and various organic chloramines

You need to be aware that our approach is somewhat unconventional because most folks lump monochloramine (NH_2Cl) into the combined chlorine group. While the conventional approach is technically more accurate than the one we are using, the conventional one is less useful because our approach helps us distinguish our target disinfectants (mono and FAC) from all the other chlorine species that might be present in the treated water.

WEIGHT-BASED UNITS OF MEASUREMENT

The chemical equations on page 1 illustrate the molecular ratios of the different molecules or ions involved in the chloramination process. However, we measure chemical feed rate in units of pounds per day (ppd) and chemical concentration in units of mg/L rather than in units of molecules/L (or more accurately moles/L). Consequently, we have to convert a molecular-based system of measurement to a weight-based system of measurement in order to calculate dosage and feed rate. This conversion is accomplished using atomic and molecular weight. For example:

Atom	Atomic Weight	Molecule	Molecular Weight
Chlorine	35	Chlorine (Cl_2)	71
Nitrogen	14	Ammonia (NH_3)	17
Hydrogen	1	Monochloramine (NH_2Cl)	51
		Dichloramine (NHCl_2)	85
		Trichloramine (NCl_3)	119

This table shows us that 71 lbs of chlorine gas (Cl_2) contains the same number of molecules as 17 lbs of ammonia, 51 lbs of monochloramine, etc. This is critical information because, when we add it to the

information obtained from the chemical equations on page 1, it tells us that adding 71 lbs of chlorine to water containing 17 lbs of free ammonia allows us to maintain the 1:1 ratio between the free chlorine and ammonia molecules that we want to maintain when forming monochloramine.

WEIGHT-BASED RATIOS

As the equations on page 1 indicate, one molecule of chlorine will produce the one chlorine atom needed to react with one ammonia molecule to form one monochloramine molecule. The equations also show that each molecule of ammonia contains one nitrogen atom. Therefore, when forming monochloramine, the ratio between the number of chlorine molecules and the number of ammonia molecules (1:1) is the same as it is for chlorine and nitrogen (also one chlorine molecule for every nitrogen atom). However, ammonia has three hydrogen atoms attached to its nitrogen atom so it weighs more than nitrogen alone. Since the weight-based ratio depends on the weight of each molecule, the weight-based chlorine-to-ammonia ($\text{Cl}_2:\text{NH}_3$) ratio will be different than the weight-based chlorine-to-nitrogen ($\text{Cl}_2:\text{N}$) ratio.

Before we can evaluate how things really work, we need to understand how things would work in a perfect world. In our imaginary little world, the optimum weight-based $\text{Cl}_2:\text{NH}_3$ ratio and the optimum weight-based $\text{Cl}_2:\text{N}$ ratio are controlled only by the molecular reactions and the weight of the molecules and atoms that participate in those reactions.

In the case of the chlorine:ammonia ratio, a 1:1 molecular ratio results in a 4.2:1 weight-to-weight ratio between chlorine and ammonia as indicated in the following equation.



In the case of the chlorine:nitrogen ratio, a 1:1 molecular ratio results in a 5.06:1 weight-to-weight ratio between chlorine and nitrogen as indicated in the following equation.



In our imaginary world, operating at different ratios would result in less than optimum results. For example:

$\text{Cl}_2:\text{NH}_3$

- $\text{Cl}_2:\text{NH}_3 < 4.2:1$
 - NH_2Cl formed
 - Excess NH_3 present after reaction
- $\text{Cl}_2:\text{NH}_3 > 4.2:1$
 - Excess Cl_2
 - NHCl_2 and NCl_3 formed
- NH_2Cl is dominant at $\text{Cl}_2:\text{NH}_3 \leq 4.2:1$
- NHCl_2 is dominant at $4.2:1 \leq \text{Cl}_2:\text{NH}_3 \leq 7.6:1$
- NCl_3 is dominant at $\text{Cl}_2:\text{NH}_3 > 7.6:1$

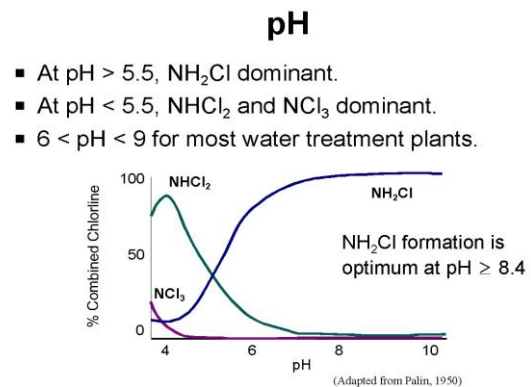
$\text{Cl}_2:\text{NH}_3$ (as N)

- $\text{Cl}_2:\text{N} < 5.1:1$
 - NH_2Cl formed
 - Excess NH_3 present after reaction
- $\text{Cl}_2:\text{N} > 5.1:1$
 - Excess Cl_2
 - NHCl_2 and NCl_3 formed
- NH_2Cl is dominant at $\text{Cl}_2:\text{N} \leq 5.1:1$
- NHCl_2 is dominant at $5.1:1 \leq \text{Cl}_2:\text{N} \leq 9.3:1$
- NCl_3 is dominant at $\text{Cl}_2:\text{N} > 9.3:1$

In these examples, the symbol $<$ means “less than” and the symbol $>$ stands for “greater than”. Similarly, the symbols \leq and \geq mean “less than or equal to” and “greater than or equal to”, respectively.

In the real world, the chemical reaction is not only affected by the chlorine:ammonia ratio but also a variety of other factors that include pH, temperature, chlorine demand, and competing reactions. Although we will address some of these issues again later, let's look at how pH can affect the rates of the chemical reactions shown on page 1.

The figure to the right indicates that low pH conditions encourage the formation of dichloramine and trichloramine, even if we have the correct $\text{Cl}_2:\text{NH}_3$ ratio. As the figure shows, trying to form monochloramine at a pH below about 6 can result in higher levels of dichloramine formation. Basically, it is better for us to try to avoid trying to form monochloramine in parts of the plant (like the rapid mix) where we are trying to suppress the pH in order to improve particle and TOC removal. If we are going to use monochloramine as a predisinfectant, we need to add the chlorine and ammonia either before or after our alum injection point.



Higher dichloramine formation rates can also occur if chlorine is applied immediately upstream of the ammonia. The chlorine solution that we inject into the water is often highly concentrated (4000 mg/L or more). Unless we are using a buffered bleach, the chlorine solution usually has a very low pH because it contains a mixture of hydrochloric and hypochlorous acids, especially if we are using gas chlorine. At the application point, the chlorine solution can consume all of the alkalinity in the water and it may take a few seconds for the chlorine solution to disperse enough to allow the alkalinity in the rest of the water to react and restore a more neutral pH. Although this situation probably occurs in most natural waters, we should expect it to be a more significant problem in low alkalinity water. This phenomena may be one of the reasons that some books indicate that the chlorine injection point should be located 5 – 10 feet upstream of the ammonia injection point if chlorine is applied first.

In our imaginary world, monochloramine is an extremely stable molecule and its level will remain constant for several weeks if we store it in a sealed, refrigerated vessel. In the real world, a variety of conditions can result in monochloramine decay. The figure to the right indicates some of the things that can cause monochloramine decay.

Chloramine Decay

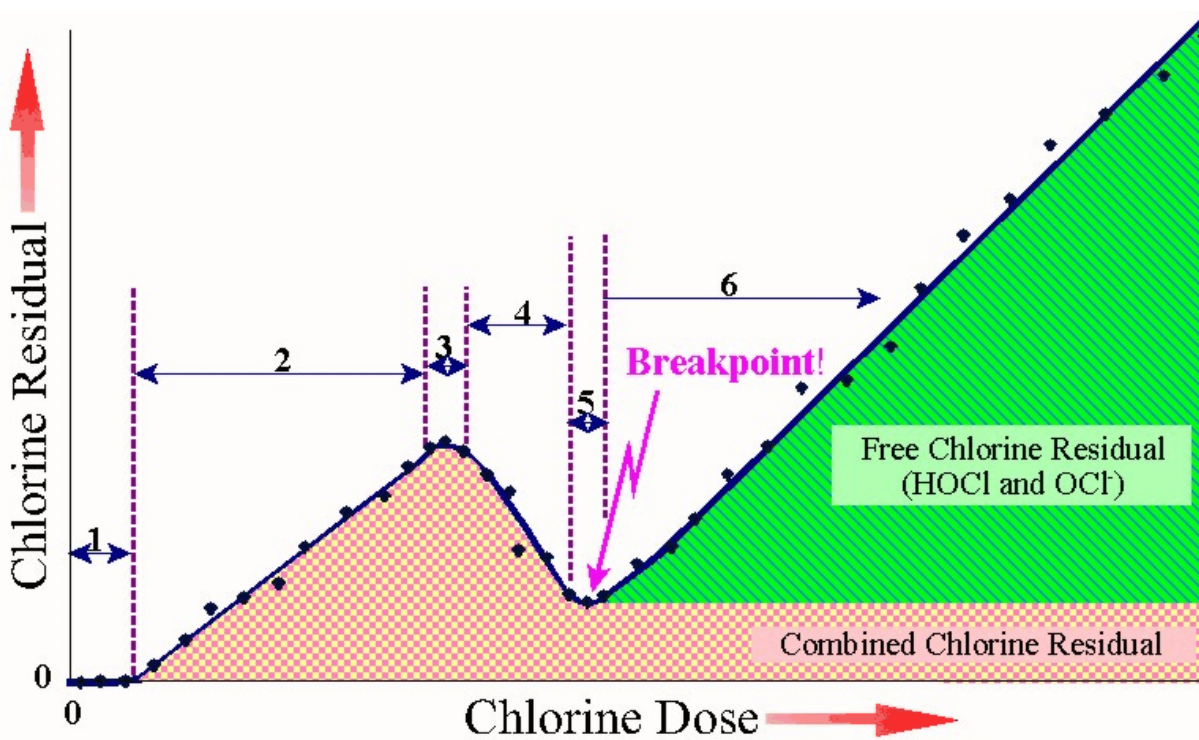
- Chloramine decay can result from
 - Autodecomposition
 - (lower pH = faster decay)
 - Oxidation of natural organic matter
 - (more NOM = faster decay)
 - Consumption by nitrifying bacteria
 - (more ammonia = more nitrifying bacteria = faster decay)
 - Oxidation of iron (including iron pipe surfaces) and other distribution materials
 - (more demand = faster decay)

THE BOTTOM LINE

We have to convert our molecular-based system of measurement to a weight-based system of measurement when we discuss tests results, dosage calculations, and feed rate measurement. However, either system of measurement leads us to the same (theoretical) conclusions about the chemistry of chloramination.

3. Free chlorine and free ammonia cannot exist in the same sample for very long.
4. **One unit of free chlorine will produce one unit of monochloramine.**
5. In theory, free chlorine and monochloramine cannot exist in the same sample for very long. (In the real world, we might get a trace of free chlorine in a sample containing mostly monochloramine or a trace of monochloramine in a sample containing mostly free chlorine.)
6. If we don't mix chlorine and ammonia in the right ratios, we will either end up with left over ammonia or end up destroying some of the monochloramine we made.
7. In theory, the right weight-based $\text{Cl}_2:\text{NH}_3$ ratio is 4.2:1 while the right $\text{Cl}_2:\text{N}$ ratio is 5.06:1.
8. If we mix chlorine and ammonia at the right ratio, the total chlorine level will neither increase nor decrease since all we are doing is converting the free chlorine to monochloramine and both of these molecules are measured by the total chlorine test.
9. In reality, a number of environmental conditions can influence our chemical reaction rates and the stability of our disinfectant. We need to consider these factors when we design and operate our chloramination facilities.

CHAPTER 2: UNDERSTANDING THE BREAKPOINT CURVE



Breakpoint chlorination is a complex process that involves a variety of competing chemical reactions that are occurring simultaneously. Although all of the reactions begin the moment that chlorine is added to the water, some of these reactions occur rapidly while others occur slowly. Consequently, the reactions that dominate in Stage 2 of breakpoint chlorination actually begin in Stage 1. Similarly, some of the reactions that dominate in Stage 1 might continue well into Stage 2 or maybe even Stages 3 or 4. Nevertheless, the following is a reasonable (but admittedly grossly oversimplified) description of what happens during each stage of breakpoint chlorination.

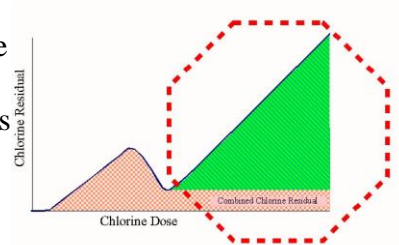
1. Readily oxidizable, simple components (soluble iron, soluble manganese, nitrite, hydrogen sulfide, etc) present in source water consume chlorine. Total chlorine residual is 0.0 mg/L (or very close to it).
2. Chlorine reacts with organic and inorganic nitrogen in source water; chloramines (including monochloramine) are formed. Total chlorine residual rises and false-positive free chlorine residuals might be detected. Usually, a 1.0 mg/L increase in the chlorine dose will produce less than a 1.0 mg/L increase in the total chlorine residual because some of the chlorine is reacting with organic nitrogen and some of the reactions in stage 1 will continue into stage 2.
3. Transition zone - total chlorine residual created and destroyed at same rate; NH_2Cl (monochloramine) starts turning into NHCl_2 (dichloramine).
4. Total chlorine residual is being destroyed at a faster rate than it is forming; NHCl_2 is being formed and destroyed and NCl_3 (trichloramine) begins to form.
5. **Breakpoint** - almost all of the available nitrogen has been oxidized; a long-lasting free chlorine residual begins to persist.
6. Free chlorine residual increases; NHCl_2 , NCl_3 , and organic chloramines may also present but most (if not all) of the monochloramine is gone. A 1.0 mg/L increase in the chlorine dose will produce close to a 1.0 mg/L rise in both the free and total chlorine residuals.

One of the benefits of the breakpoint curve is that we can use it to help us understand the chloramination process and interpret the results of our laboratory tests. The breakpoint curve allows us to visualize where we are in the process and what adjustments we need to make to optimize our disinfection process. Let's consider the two disinfection scenarios that operators are likely to use on a routine basis.

SCENARIO 1: CHLORINE IS ADDED BEFORE AMMONIA

NOTE: This is the sequence that chlorine and ammonia must be applied if you are disinfecting untreated water with chloramines.

In this scenario, we want to add enough chlorine to go past the breakpoint and move far enough up the free chlorine curve so that, when we add the ammonia, we get the monochloramine residual we want. This way we can oxidize iron, manganese, sulfide and some of the organic nitrogen. As the breakpoint curve to the right indicates, the process will also allow us to determine about how much difference there will probably be between our monochloramine and total chlorine residuals.



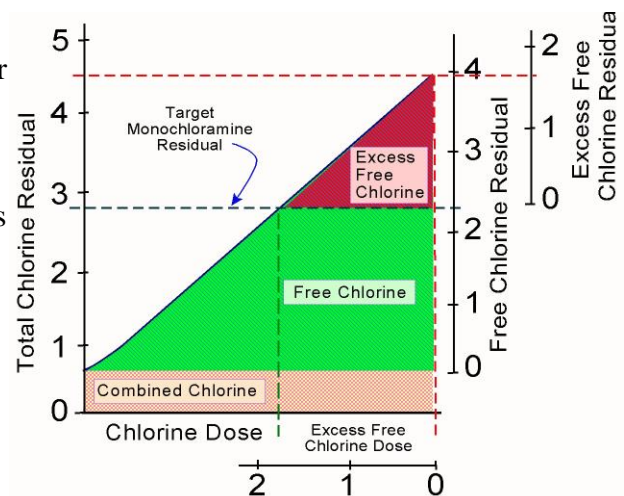
Let's assume that we want to achieve a monochloramine residual of about 2.3 mg/L or so. Let's also assume that our current operating conditions produce the following results:

TAC = 4.6 mg/L FAC = 4.0 mg/L Mono = trace mg/L FAA = 0.0 mg/L as NH_3

Question 1: What does the data tell us about our conditions?

The data indicates that:

- 1) Our current chlorine dose produces a free chlorine residual that is 1.7 mg/L higher than our target monochloramine level.
10. We will need to lower the chlorine feed rate enough to drop the free chlorine residual to our 2.3 mg/L monochloramine target. As the curve indicates, there is a 1:1 relationship between chlorine dose and residual once we have reached breakpoint. Therefore, a 1.0 mg/L change in chlorine dose results in a 1.0 mg/L change in the free chlorine residual.
11. Our total chlorine residual is 0.6 mg/L higher than our free chlorine residual.
12. If we make the right adjustments, the total chlorine residual will probably remain about 0.6 mg/L higher than our monochloramine residual because:



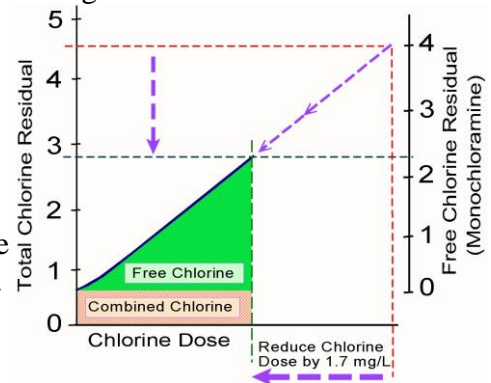
- a) although the total chlorine test kit measures all forms of chloramines (including some organic chloramines), the monochloramine test kit only measures monochloramine;
- b) the combined chlorine will contain very little mono chloramine since the monochloramine and free chlorine cannot coexist; and
- c) adding ammonia does not affect the combined chlorine that formed during the breakpoint chlorination process.

Question 2: What will happen if we reduce our chlorine dose by 1.7 mg/L?

When we reduce the chlorine dose:

- 1) Our free chlorine residual will drop from 4.0 mg/L to 2.3 mg/L (our target monochloramine residual).
- 2) Our total chlorine residual will drop from 4.6 mg/L to 2.9 mg/L (because the combined chlorine that was formed during breakpoint chlorination will still be there).

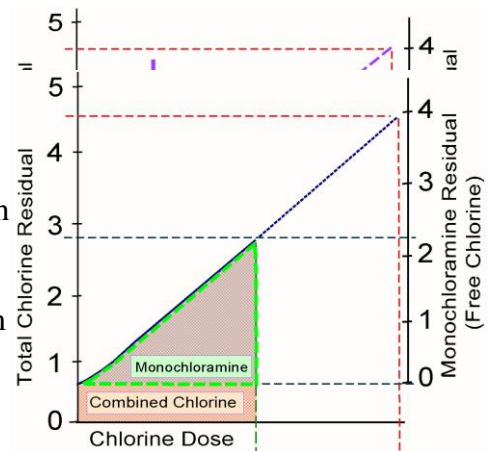
In essence, we want to slide back down the free chlorine part of the breakpoint curve until we reach our 2.3 mg/L free chlorine target.



Question 3: What will happen if add the right amount of ammonia after reducing our chlorine dose by 1.7 mg/L?

Once we add the right amount of ammonia:

- 1) our 2.3 mg/L of free chlorine will combine with the ammonia to form 2.3 mg/L of monochloramine;
- 2) our total chlorine residual will remain at about 2.9 mg/L because all we did was convert the free chlorine to monochloramine and the total chlorine tests measures both kinds of molecules; and
- 3) in theory, our free chlorine residual will drop to 0.0 mg/L or so because it will be reacting with the ammonia to form monochloramine. (In the real world, we often get a positive free chlorine test because monochloramine will interfere with the DPD method and give a false positive reading.)

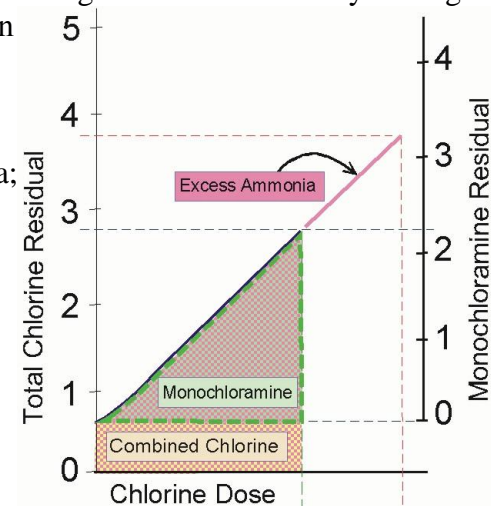


Question 4: What will happen if add the too much ammonia after cutting our chlorine dose by 1.7 mg/L?

In this case, chlorine is the “limiting reactant” because we will run out of free chlorine before all the ammonia has reacted.

Therefore:

- 1) we will get the same total chlorine and monochloramine residuals we would get if we hadn’t fed too much ammonia;
- 2) we will have unreacted ammonia which means that:
 - a) we could end up having a problem with biofilm in the distribution system because some bacteria use free ammonia as a food source,
 - b) if a biofilm bacteria get established, we could have trouble maintaining a chloramine residual in distribution because the bacteria exert a chlorine demand and can be difficult to completely eliminate; and

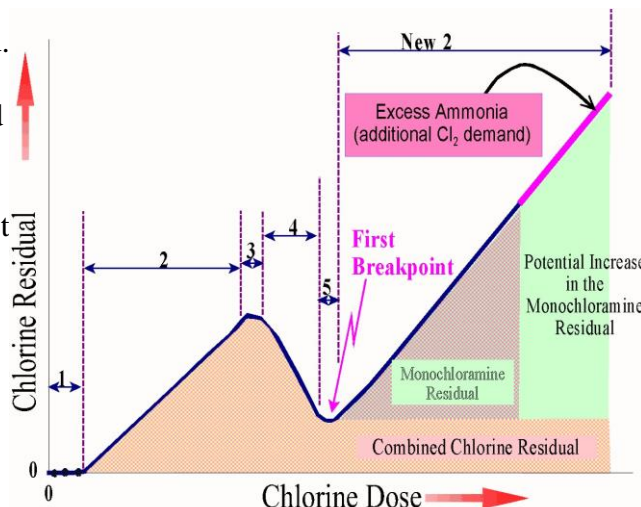


- we extend the breakpoint curve (or more accurately, extend a **new** breakpoint curve) so that both the total chlorine and monochloramine residuals would go up if we add more chlorine. How far up the curve we could go depends on how much excess ammonia we put in and then how much additional chlorine we apply to form additional chloramine.

Question 4b: Why does adding ammonia effectively begin a new breakpoint curve?

As soon as we consume all of the available free chlorine, we have basically created a new section 2 of the breakpoint curve (on page 7) because we have created an additional chlorine demand. However, in this case:

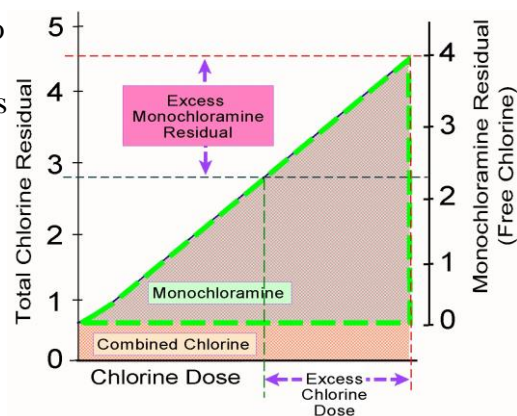
- there should be no chlorine demand due to readily-oxidizable compounds because they will have been completely oxidized when first added chlorine; and
- there should be very little demand from organic ammonia since it was satisfied when we went through breakpoint the first time; and
- (therefore) a 1.0 mg/L increase in the chlorine dose should produce about a 1.0 mg/L increase in the total chlorine and monochloramine residuals . . . at least until we run out of either chlorine or ammonia. In the real world, we may find that we have to add slightly more than 1.0 mg/L of chlorine to produce 1.0 mg/L of monochloramine because competing reactions (such as dichloramine formation) will consume some of our chlorine.



Question 5: What will happen if we do not lower the chlorine feed rate but add enough ammonia to tie up all the free chlorine?

Three things will happen if we add enough additional ammonia to tie up all the free chlorine,

- the monochloramine residual will rise to about 4.0 mg/L as the free chlorine reacts with the ammonia;
- the free chlorine residual will drop to almost 0.0 mg/L at the same rate that the monochloramine residual increases (because 1.0 mg/L of free chlorine turns into 1.0 mg/L of monochloramine); and
- the total chlorine residual will remain at about 4.6 mg/L since total chlorine test measures both combined chlorine and monochloramine.



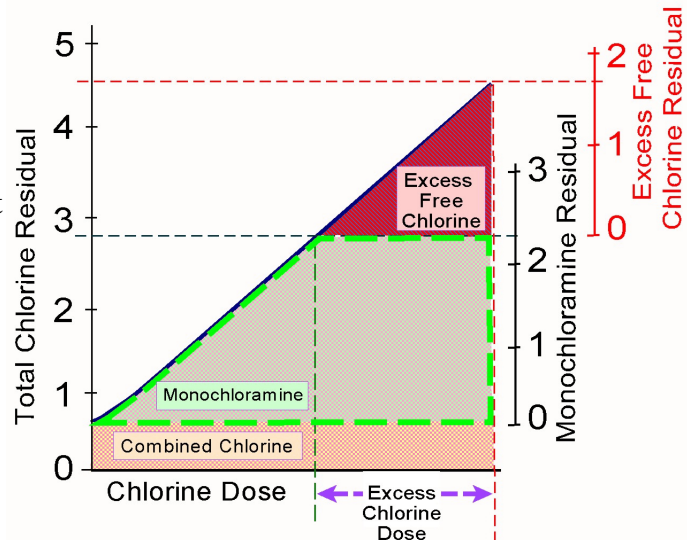
If we added even more ammonia, we'd end up with the potential for extending the breakpoint curve just as we did in Question 3. However, this extension would begin at the 4.0 mg/L monochloramine point because that's where we ran out of chlorine.

Question 6: What will happen if we don't reduce the chlorine feed rate before we add the right amount of ammonia?

In this case, ammonia becomes the “limiting reactant” because we will run out of ammonia before all of the chlorine has reacted. However, as we discussed previously, monochloramine and free chlorine cannot coexist at any significant concentration for a significant period of time because the excess chlorine will react with monochloramine to form di- and trichloramine. Therefore, if we add the proper amount of ammonia without reducing the chlorine dose, we will probably see several things happen.

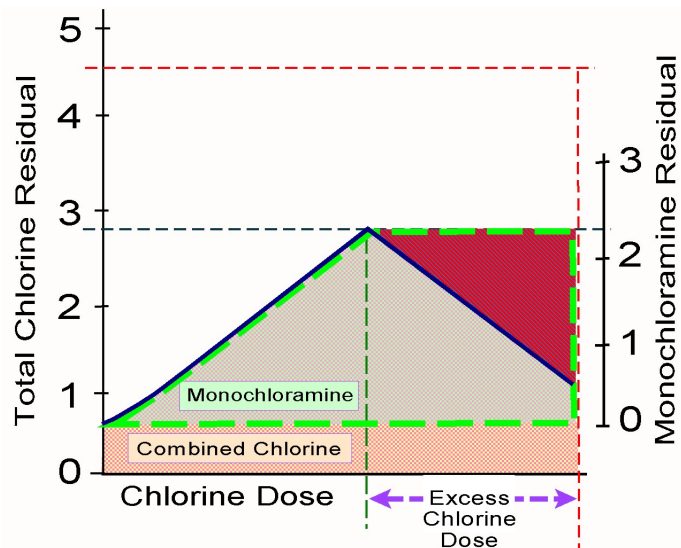
Initially, we will find that:

- 1) the free chlorine level will rapidly drop from 4.0 mg/L to 1.7 mg/L as it reacts quickly with the free ammonia; and
- 4) the monochloramine level will simultaneously rapidly rise to our target level (of 2.3 mg/L) as the ammonia and chlorine react.



Since monochloramine and free chlorine cannot coexist to any significant degree, chemical reactions will continue until all (or almost all) of the free chlorine is consumed. Consequently, as the reaction continues we will see that:

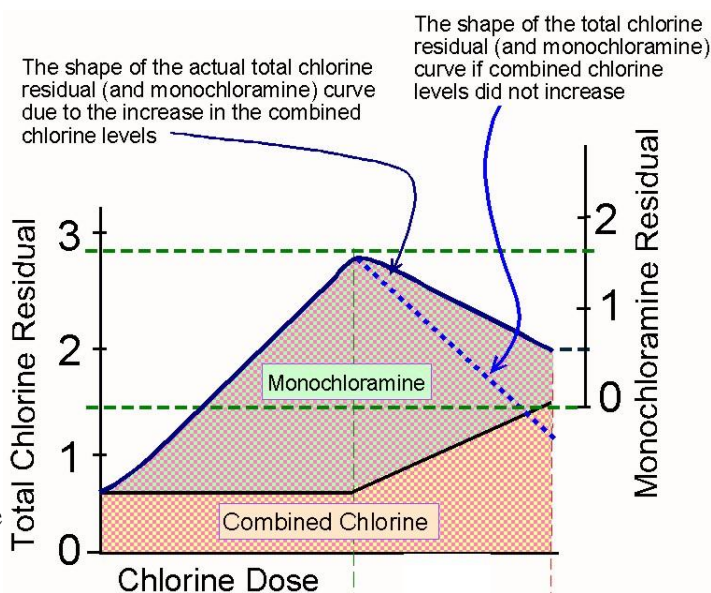
- 5) the free chlorine level will continue to drop from 1.7 mg/L to 0.0 mg/L as it reacts with the monochloramine to form dichloramine and with the dichloramine to form trichloramine;
- 6) the monochloramine residual will start to fall as the excess chlorine converts it to di- and trichloramine;
- 7) the monochloramine residual will probably not drop to zero since we will run out of excess chlorine before the mono is converted entirely to di- and trichloramine;



Using the breakpoint curve, we can see that what has happened is that we have basically flipped the “Excess Free Chlorine” part of the graph over and covered part of the “Monochloramine” section of the graph. By doing this, we can illustrate that the free chlorine is reacting with monochloramine. However, this figure does not show the whole picture because it does not show what happens to the monochloramine once it is converted to dichloramine or trichloramine.

In reality, we will probably see a few more things happen:

- 8) the point on the breakpoint curve is more rounded than pointed because the destruction of monochloramine actually begins before all the ammonia is consumed;
- 9) the monochloramine residual may not actually reach our target of 2.3 mg/L because of this destruction;
- 10) the combined chlorine level will begin to increase when the destruction of mono begins;
- 11) the monochloramine residual will probably fall faster than the total residual because the monochloramine test does not detect di- and trichloramine while the total test kit does; and
- 12) the difference between the monochloramine and total chlorine residuals will gradually increase to greater than 0.6 mg/L.

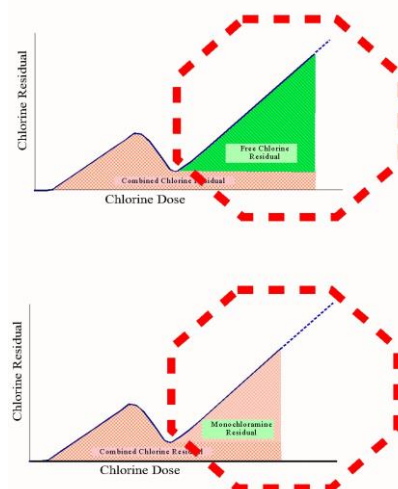


The actual data (and therefore the shape of the curve) we get will vary based on a lot of factors that we will discuss later. In this illustration, monochloramine destruction began long before we reached 2.3 mg/L. By the time the reaction was complete, the monochloramine residual was only 0.5 mg/L (or -1.8 mg/L) but only dropped the total chlorine to 1.5 mg/L (or -1.4 mg/L). As a result, the difference between monochloramine and total chlorine rose to 1.0 mg/L.

SCENARIO 2: AMMONIA IS ADDED BEFORE CHLORINE

NOTE: This is the sequence that chlorine and ammonia should be applied if you are boosting the disinfectant residual in water that has already been treated with free chlorine, chlorine dioxide, or ozone. It should not be used to disinfect untreated water.

In the second scenario, we (or our treated water wholesaler) used chlorine, chlorine dioxide, or ozone to meet the oxidant demand and establish a measurable free chlorine, chlorine dioxide, or ozone residual in the water. We just want add enough chlorine and ammonia to complete the disinfection process or to raise the chloramine level before we send the water to distribution. In this case, we want to add ammonia before we add chlorine. By adding ammonia first, we minimize the chance the chlorine we are adding will react with (destroy) the monochloramine that we are forming or that is already in the water.



In this scenario, let's assume that we want to achieve a monochloramine residual of about 2.3 mg/L or so. Current operations produce the following data:

TAC = 2.3 mg/L FAC = 0.0 mg/L Mono = 1.6 mg/L FAA = 0.2 mg/L as NH₃

The first question we need to ask ourselves is: Do we need to add more ammonia or is there already enough present to get us to our target monochloramine residual of 2.3 mg/L if we just add chlorine. This is a question similar to the one that we should have asked ourselves in Scenario 1. What is “the right amount of ammonia for a 2.3 mg/L free chlorine residual”?

The second question we need to ask ourselves is: Once we have the right amount of ammonia, how much chlorine do we need to add to reach our target monochloramine residual?

To answer these questions in practical terms, we need to understand the difference between molecular-based measurements (such as the chemical equations shown on page 1) and weight-based units that we use at the plant on a daily basis.

WE'LL GET BACK TO THE SECOND SCENARIO LATER

THE BOTTOM LINE

- 1) The breakpoint chlorination curve helps us visualize what will happen during the various stages of the chloramination process.
- 2) We need to be able to measure free available chlorine, total available chlorine, monochloramine, and free available ammonia.
- 3) We can use our FAC, TAC, monochloramine, and FAA data to figure out where we are on the curve and what general adjustments we need to make to get where we want to be.
- 4) The TAC residual should not change simply because we add ammonia . . . if we add enough ammonia to combine with all of our FAC.
- 5) However, if we have too much FAC present after we add our ammonia,
 - a) our monochloramine will be lower than we expected,
 - b) our TAC residual will drop, and
 - c) our combined chlorine level will increase (the difference between monochloramine and TAC will be greater than the difference between FAC and TAC).
- 6) Chlorine, chlorine dioxide, or ozone needs to be added to undisinfect water before we add our ammonia.
- 7) Ammonia should be added before chlorine if we are boosting the chloramine residual in water that has already been disinfected with free chlorine, chlorine dioxide, or ozone.
- 8) Competing reactions (such as dichloramine formation) can affect the shape of our breakpoint curve. In addition, these competing reactions may mean that we have to add slightly more than 1.0 mg/L of chlorine to get 1.0 mg/L of monochloramine when we are boosting chlorinating water that contains a free ammonia residual.

CHAPTER 3:

UNDERSTANDING WEIGHT-BASED DOSAGE AND FEED RATE CALCULATIONS

In simple terms, chemical dose is the amount of chemical that we put into the water divided by the amount of water we put it into. Similarly, the chemical feed rate is simply the amount of chemical that we put into the water divided by the amount of time it took us to add it. However, dosage and feed rate are actually somewhat complicated issues because:

- 1) dosage and feed rate calculations can be influenced by a variety of competing reactions;
- 9) the amount of time that is available for competing reactions to occur affects the amount of chlorine that is available to react with our free ammonia;
- 10) our ability to evaluate and control the chloramination process is affected by the accuracy of our free chlorine, total chlorine, monochloramine, and free ammonia analytical methods and by our ability to properly interpret and apply the test results;
- 11) we need to understand the concept of parts per million (ppm) and how it relates to chemical dosage and feed rates; and
- 12) dosage and feed rate calculations depend on the molecular formula and the concentration of the chemical we are using since different materials contain different amounts of chlorine and ammonia.

COMPETING REACTIONS

As noted previously, chemical reactions can occur simultaneously. However, some reactions will occur faster than others. A variety of factors (such as the pH and temperature of the solution and the relative concentration of the reactants and products) influence reaction rates. For example, the breakpoint curve indicates that chlorine will react with strong reducing substances such ferrous iron and hydrogen sulfide much faster than it reacts with organic ammonia. Similarly, free chlorine will react with free ammonia before it will react with monochloramine. However, if the free ammonia concentration is low and the monochloramine concentration is high, the reaction with monochloramine may dominate simply because there are many more monochloramine molecules present than there are free ammonia molecules. Although the chlorine would prefer to react with ammonia, it will react with whatever is present if it can't find an ammonia molecule.

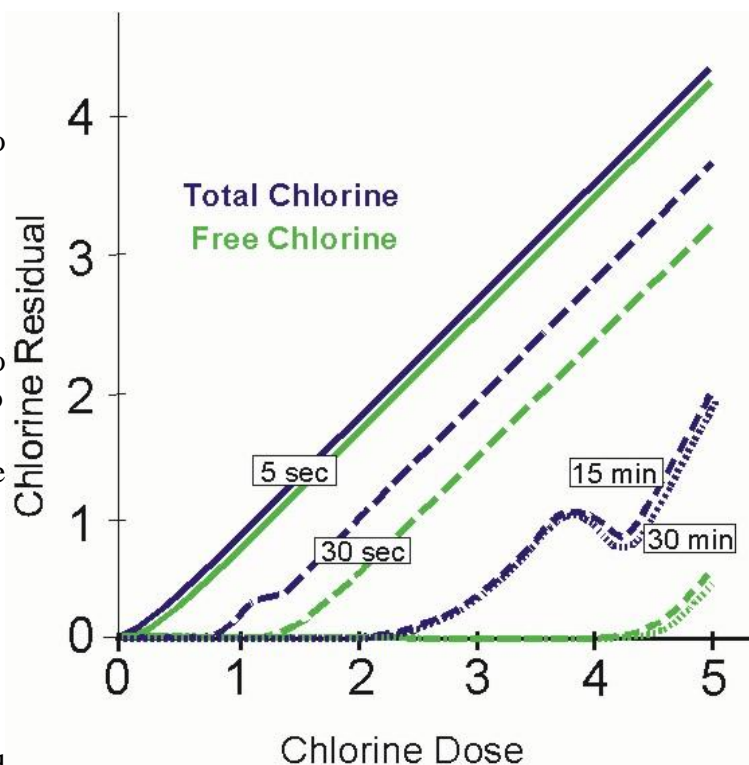
It is sometimes difficult to precisely anticipate the impact of competing chemical reactions that can consume some of the chlorine before free chlorine begins to form or that can result in the decay of the monochloramine once it has formed. Therefore, it's not enough to just know how much chemical we add. We also need to be able to measure how much of the chemical we add is present after the competing reactions have consumed some of it. This is particularly important when we deal with free chlorine because there are a lot of competing reactions and a lot of these reactions can occur within 1–2 minutes (and many can occur within a few seconds). It's not so important when we deal with free ammonia because there are not many competing reactions that will consume our ammonia.

AVAILABLE REACTION TIME

The available reaction time is also an important issue because it impacts the amount of free chlorine that is available to react with our free ammonia. More reaction time not only means that each competing reaction moves further toward completion but that more types of (slower) reactions can begin and end before we add the ammonia.

The figure to the right illustrates the impact that (competing reaction) reaction time has on the total and free chlorine residual. In the figure, we see that:

- 1) if we stop the reaction after just a few seconds,
 - a) there has been very little chlorine demand because relatively few competing reactions have had time to progress very far, and
 - b) the free and total chlorine levels will be pretty much the same;
- 13) if we allow the competing reactions to proceed for about 30 seconds,
 - a) reducing substances will have time to consume some of the chlorine and so we see the Stage 1 response that we saw on the breakpoint curve (on page 7),
 - b) chlorine has begun to react with organic and inorganic nitrogen and produced a small blip in the curve (that is similar to the Stage 2 response shown on the breakpoint curve on page 7) but there hasn't been enough time for the Stage 2 and Stage 3 reactions to proceed very far, and
 - c) the total and free chlorine residuals will be lower than they would have been if we terminated the competing reactions after only a few seconds;
- 14) if we allow the competing reactions to occur for several minutes (usually 10 – 15 or more),
 - a) the curve looks pretty much like the breakpoint curve shown on page 7 because all (or almost all) of the reducing substances and most of the initial reactions with organic and inorganic ammonia have reacted with chlorine,
 - b) although some Stage 4 reactions will continue if the reaction time is increased, the shape of the curve has become very stable (i.e., doesn't change much if the reaction time is further increased), and
 - c) the total and free chlorine residuals don't change much after 10 – 15 minutes unless we introduce a new source of demand.



As the figure above suggests, competing reactions and available reaction time can also impact our ability to obtain and interpret test data. For example, if we are adding ammonia a couple of feet downstream of our chlorine, we do not have time to collect the sample and run the free chlorine test before the sampling and analytical time exceeds the time that the competing reactions can occur before the ammonia reacts with the chlorine.

ANALYTICAL METHODS

To effectively evaluate and control our chloramination process, we need to be able to accurately measure total chlorine, free chlorine, monochloramine, and free ammonia. Consequently, we need be aware of some issues that can influence our tests results. For example:

- 15) Monochloramine can falsely elevate the free chlorine reading when using the DPD test. Because of this interference, we should not use the DPD free chlorine method when we know that the monochloramine residual is above 0.5 mg/L or so. We should be especially suspicious of any free chlorine reading we get when the free ammonia level is 0.1 mg/L or higher because free chlorine and free ammonia cannot coexist for very long.
- 16) Although many nitrogen-containing compounds can react with free chlorine, only free ammonia reacts to form our target disinfectant, monochloramine. Therefore, we must be able to distinguish between free and total ammonia just as we must be able to distinguish between free and total chlorine. Consequently, we need to use a free ammonia method that will only detect free ammonia and not all forms of nitrogen (e.g., nitrate, nitrite, or urea and organic molecules containing amine groups).
- 17) When we are adding ammonia, we must also be able to distinguish between monochloramine (our target disinfectant) and other chloramine species, i.e., total chloramines. The most common total chlorine method (DPD) measures all of the chloramine species. While the total chlorine residual is an useful piece of information, we must be able to measure monochloramine in order to control the disinfection process.

Although analytical methods are all based on the molecular reactions that occur during the analysis, the results are reported in a weight-based units, such as mg/L, rather than on a molecular basis, such as moles/L. Since the weight-based result (mg/L) depends on the weight of each molecule (and not just the number of molecules), weight-based results depend on how the results are reported.

Compound and Concentration	Molecular Formula	Molecular Weight	Reported Result ⁽¹⁾
0.1 millimoles of monochloramine (NH ₂ Cl)	Cl ₂	71	7.1 mg/L as Cl ₂
	NH ₂ Cl	51.5	5.15 mg/L as NH ₂ Cl
	N	14	1.4 mg/L as N
0.01 millimoles of free available ammonia (NH ₃ as NH ₃)	NH ₃	17	0.17 mg/L as NH ₃
	N	14	0.14 mg/L as NH ₃ -N

(1) These values are obtained by multiplying the molecular concentration of the compound we are testing for by the molecular weight of the compound that we are reporting in.

As the table above indicates, we cannot properly interpret our results unless we know how our instrument is reporting them. For example, since ammonia weighs 21% more than nitrogen, not knowing what units our test kit is reporting can produce a 21% error in our calculations.

Some instruments (like Hach's DR850, DR890, DR4000, and DR5000) allow us to select how we want our results reported (e.g., mg/L as NH₃ or mg/L as NH₃-N). Other instruments (like Hach's Free Ammonia/Monochloramine colorimeter and their Chlorine colorimeter) will only report values one way.

Unless there is a good reason to choose an alternate way of reporting, the TCEQ suggests that we report our monochloramine results as “mg/L as Cl₂” and our free ammonia results as “mg/L as NH₃”. This approach allows us to easily compare the free chlorine, total chlorine, and monochloramine results since all the disinfectant levels will be reported in the same units. Similarly, reporting ammonia levels as “mg/L NH₃” is helpful because NH₃ is the molecule that reacts with chlorine to form ammonia. If your ammonia test kit only allows you to report ammonia level as “mg/L of NH₃-N”, you will need to multiply your reading by 1.21 to convert the reading to “mg/L of NH₃” since ammonia weighs 21% more than nitrogen.

PARTS PER MILLION

Except for a few cases (usually involving proprietary liquid coagulants), we should always describe our chemical dose on a weight-to-weight (^{w/w}) basis. Since we are dealing with relatively low chemical levels, we usually describe our chemical dose in terms of parts of chemical per million parts of water (ppm). For example, we often describe the dose in terms of pounds of chemical per million pounds of water or milligrams of chemical per million milligrams of water (which is the same as mg/L since one liter of water weighs a million milligrams). It is important to understand that, on a weight-basis, 1 ppm = 1 lb per 10⁶ lbs = 1 mg/L as shown below:

By definition, 1 ppm (^{w/w}) = 1 pound of chemical per million (10⁶) pounds of water.

1.0 lb = 454 g

Therefore, 1 ppm = 454 g per 10⁶ lbs of water.

1.0 g = 1,000 mg

Therefore, 454 g per 10⁶ lbs of water = 454,000 mg per 10⁶ lbs of water

1.0 gallon of water weighs 8.34 lbs

Therefore, 10⁶ lbs of water = 1,000,000/8.34, or 119,900 gallons of water

and

Therefore, 454,000 mg per 10⁶ lbs of water = 454,000 mg per 119,900 gallons of water

1.0 gallon = 3.785 L

Therefore,

454,000 mg per 119,900 gallons of water = 454,000 mg per 454,000 L of water, or 1.0 mg/L

and we just proved that 1.0 ppm = 1 lb/10⁶ lbs = 1 mg/L

Although we can also use the term “ppm” to describe a volumetric dose (such as gallons of liquid chemical per million gallons of water), we should probably avoid that approach since liquid chemicals are usually dilute solutions of a pure chemical and we need to know what our actual chemical dosage is rather than the solution dosage we are applying.

MOLECULAR FORMULA AND CHEMICAL CONCENTRATION

Chemical dose and feed rate calculations must address the molecular formula and concentration of the chemical being applied. Many of the chemicals that we feed at the plant are molecular compounds that contain the materials other than the molecular group that we need to apply. This is particularly true when we are feeding liquid chemicals because these chemical solutions typically contain lots of water. As a result, there may be a difference between chemical dose and reactant dose.

If the chemical we are applying contains only the molecular group that participates in the reaction we want to achieve, the chemical dose and the reactant dose are equal. For example, chlorine gas and ammonia gas contain very little other material other than chlorine and ammonia, respectively. Consequently, the chemical and reactant doses are equal when we use these chemicals.

However, if the chemical that we apply is a chemical compound or solution, only part of what we add actually participates in our reaction. For example, liquid ammonium sulfate contains a sulfate group which does not participate in the chloramination process. In addition, it is a solution and, therefore contains even less ammonia than pure ammonium sulfate. As a result, we have to apply more of the chemical than we would if it only contained the reactant that we need.

As previously noted, competing chemical reactions can consume some of the reactants that we apply. Therefore, we also need to understand the difference between the terms “applied dose” and “effective dose”. The applied dose is equal to the amount of chemical we actually add to the unit of water while the effective dose is the amount of reactant that remains (after competing reactions consume some of it) to form the products that we want to form.

Sometimes, there is an important difference between the applied chemical dose and the effective reactant dose. For example, if we put 5 mg/L of pure chlorine into untreated water that has a 2 mg/L chlorine demand, we’ll end up with water that contains 3 mg/L of free chlorine. In this case, our applied chlorine dose was 5 mg/L but our effective chlorine dose was only 3 mg/L.

Other times, there is an almost no difference between the applied reactant dose and the effective reactant dose. For example, water usually has a very low ammonia demand. Therefore, if we put 1 mg/L of pure ammonia (as NH_3), we’ll probably end up with close to a 1 mg/L effective free ammonia (as NH_3) dose. Similarly, our effective chlorine dose will be close to 1.0 mg/L if we put 1 mg/L of pure chlorine into water that has already been disinfected and has enough ammonia to react with the chlorine (since chlorine tends to combine with the ammonia before it reacts with other materials).

CHLORINE DOSE AND FEED RATE

Chlorine is available in a variety of forms and concentrations. For example, chlorine gas contains 100% available chlorine, calcium hypochlorite is a solid form that generally contains 60-75% available chlorine, and sodium hypochlorite (bleach) is a liquid that usually contains 5-12% available chlorine. Consequently, the feed rate and dosage calculations must address both the weight of the material being applied and its concentration.

Let’s compare the chemical feed rates for a plant that wants to feed chlorine at a rate of 10 lbs per day.

Example 1: Gas Chlorine

Data: Gas chlorine contains 100% available chlorine

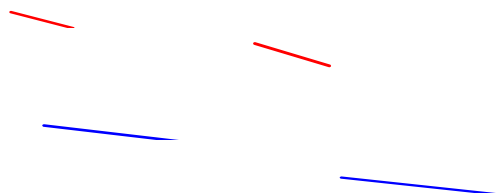
Calculation: Rotameter setting = 10 ppd (pounds per day) . . . that was easy.

Example 2: Calcium Hypochlorite

Data: Our calcium hypochlorite contains 65% available chlorine

We create our feedstock by adding 10 lbs of calcium hypochlorite to 10 gallons of water

Calculation: $1 \text{ lb Ca(OCl)}_2 \times 65\% \text{ available chlorine} = 0.65 \text{ lbs of chlorine per lb of Ca(OCl)}_2$



Example 3: Sodium Hypochlorite

Data: Our sodium hypochlorite bleach contains 10% available chlorine
Our bleach has a specific gravity of 1.28
Each gallon of water weighs 8.34 lbs

Calculation: 1 lb bleach X 10% available chlorine = 0.10 lbs of chlorine per lb of bleach

1 gallon bleach = 1.28 X 8.34 = 10.68 lbs of bleach per gallon of bleach

These three examples clearly show that:

- 1) we need to base our chemical feed rate on the pounds of reactant that we want to add . . . even if we need to figure out how many gallons of solution we need to add;
- 2) to get the amount of reactant we want, we need different amounts of chemical (in these examples we needed 10 ppd of chlorine gas, 15.4 ppd of calcium hypochlorite, or 100 ppd of sodium hypochlorite bleach to get 10 ppd of chlorine reactant); and
- 3) our chemical feed rate depended on the concentration of the reactant in the chemical we're feeding and (in the case of liquid chemicals) the weight or specific gravity of the solution.

Let's use this information from our three examples to demonstrate the difference between the applied chemical dose, the applied reactant dose, and the effective reactant dose. Let's assume that our (water) flow rate is 166 gpm (which is about 240,000 gpd, or 2.00 million ppd). Let's also assume that our raw water has a 2.0 mg/L chlorine demand (which means that the chlorine residual that we measure at our ammonia application point is 2.0 mg/L less than the chlorine dose that we applied).

	Gas Cl₂	Calcium Hypochlorite	Sodium Hypochlorite Bleach
Chemical Feed Rate (ppd) (from the example)	10	15.4	100
Water Flow Rate (million ppd)	2.00	2.00	2.00
Applied Chemical Dose (ppm of Cl ₂)	5.0	7.7	50
Reactant Feed Rate (ppd of Cl ₂)	10	10	10
Applied Reactant Dose (ppm of Cl ₂)	5.0	5.0	5.0
Chlorine Demand (mg/L of Cl ₂)	2.0	2.0	2.0
Effective Reactant Dose (ppm of Cl ₂)	3.0	3.0	3.0

AMMONIA DOSE AND FEED RATE

Ammonia, like chlorine, is available in many forms and concentrations. Consequently, the ammonia feed rate and dosage calculations must also address both the weight of the material being applied and its concentration. However, dealing with ammonia calculations is even more complex than dealing with chlorine calculations. To understand why, we need to be aware of several issues.

- 4) Different compounds contain different amounts of ammonia (and, therefore, different amounts of nitrogen). Consequently, the feed rate dosage calculations will differ depending on the type of chemical used and the number of ammonia (or nitrogen) atoms it contains.

Compound	Molecular Formula	Molecular Weight	% Available Ammonia	
			as NH ₃ ⁽¹⁾	as N ⁽²⁾
Ammonia (gas)	NH ₃	17	100%	82.4%
Ammonium hydroxide (dry)	NH ₄ OH	35	48.6%	40.0%
Ammonium sulfate (dry)	(NH ₄) ₂ SO ₄	132	25.8%	21.2%

(1) These values are obtained by dividing the weight of NH₃ (which is 17) by the molecular weight of the compound we are feeding and then multiplying that result by the number of ammonia molecules the compound contains.

(2) These values are obtained by dividing the weight of N (which is 14) by the molecular weight of the compound we are feeding and then multiplying that result by the number of nitrogen atoms the compound contains.

- 5) Anhydrous ammonia (like anhydrous chlorine) is a pure liquid that is stored in a sealed cylinder and then vaporized and fed as a gas. Other liquid ammonia compounds are more like chlorine bleach; the calculations must address the density (weight) of the solution being applied, the concentration of the solution, and the ammonia content of the compound it contains.

However, liquid ammonium sulfate (LAS) and liquid ammonium hydroxide (LAH) differ from liquid bleach in one important respect. Bleach vendors almost always express their concentration in terms of “% available chlorine on a w/w (weight to weight) basis”. LAS and LAH vendors, on the other hand, often describe their products based on the amount of dry chemical present in the solution. While one pound of a 10% bleach almost always contains about 0.10 pounds of available chlorine, a pound of 25% LAS could contain 0.25 pounds of dry ammonium sulfate, 0.25 pounds of available ammonia, or 0.25 pounds of available nitrogen.

It is extremely important to know how our vendor specs his product because an LAS solution that contains “25% ammonium sulfate on a w/w basis” only contains 6.45% available ammonia and 5.3% available nitrogen. (If the solution contains 25% AS and AS is only 25.8% NH₃, then the percent available ammonia (as NH₃) is equal to 25.8% of 25%, or 6.45%).

Let's compare the chemical feed rates for a plant that wants to feed ammonia (as NH_3) at a rate of 2 lbs per day.

Example 1: Anhydrous Ammonia

Data: Anhydrous ammonia contains 100% available ammonia

Calculation: Rotameter setting = 2 ppd NH_3 (as NH_3) . . . that was easy.

Example 2: Dry Ammonium Sulfate

We're going to skip this example because nobody in Texas is making their own LAS solution.

Example 3: Liquid Ammonium Sulfate

Data: Our LAS contains 38% ammonium sulfate on a w/w basis

Based on the molecular formulas of the two compounds, 132 pounds of ammonium sulfate (NH_4)₂SO₄ contains 34 pounds of ammonia (as NH_3)

Our LAS has a specific gravity of 1.23

Each gallon of water weighs 8.34 lbs

Calculation:

$$1 \text{ lb LAS} \times 38\% \text{ ammonium sulfate} = 0.38 \text{ lbs of pure AS per lb of LAS}$$

$$1 \text{ gallon LAS} = 1.23 \times 8.34 = 10.26 \text{ lbs of LAS per gallon of LAS}$$

{Notice that "gpd of LAS" equals "ppd of ammonia (as NH_3)" if you are feeding this chemical.}

Always remember that when we are feeding liquid chemicals, our reactant dose depends on the concentration of the reactant in our liquid and the weight (or specific gravity) of the liquid. Since the specific gravity of liquid chemicals can vary slightly, we need to be able to measure the specific gravity of each batch of chemical when it is delivered. The *hydrometer* is a simple, inexpensive instrument used to measure the specific gravity of a solution. Every plant that feeds liquid chemicals should have a hydrometer so the plant staff can measure the specific gravity.

THE BOTTOM LINE

- 6) We always have to be aware of the potential impact of competing reactions and the time that is available for these competing reactions to occur.
- 7) We need to be aware of and understand how our instruments are reporting our results so that we can interpret our data. If we have a choice, we should set our instruments to:
 - a) report FAC, TAC, and monochloramine results as “mg/L as Cl₂”, and
 - b) report FAA levels as “mg/L as NH₃”.
- 8) Chemical dose should be calculated on a weight-to-weight (^w/_w) basis whenever possible and 1 ppm (^w/_w) = 1 lb/10⁶ lbs = 1 mg/L.
- 9) It is important to understand that there is a difference between applied chemical dose, applied reactant dose, and effective reactant dose.
 - a) Applied Chemical Dose: the amount of chemical we add divided by the amount of water we put it in
 - b) Applied Reactant Dose: the amount of the reactant (contained in the chemical we add) divided by the amount of water we put it in
 - c) Effective Reactant Dose: the amount of the reactant (contained in the chemical we add) that (after any competing reactions) is actually available to form product we want divided by the amount of water we put it in
- 10) Dose and feed rate calculations depend on the molecular formula and the concentration of the material we are adding.

CHAPTER 4:

APPLYING THE CONCEPTS

We have just reviewed many of the important issues related to chloramination chemistry, analytical methods, and chemical dose and feed rate calculations. Now it's time to use the concepts to help us evaluate and control the chloramination process at our plant. Several years ago, one of the TCEQ staff members (a very wise fellow named Chuck Schwarz) gave a presentation in which he discussed a simple process control loop. This process control loop can be applied to the chloramination process in the following manner:

- 1) **Collect Data** means that, at each chemical application point, we need to gather the applicable information about:
 - a) our target FAC, TAC, and monochloramine residuals and our desired FAA level,
 - b) our current FAC, TAC, monochloramine, and FAA levels,
 - c) our current chemical feed rates and water flow rates,
 - d) the molecular weight and formula of the chemicals we use to form monochloramine, and
 - e) the concentration (on a w/w basis) and specific gravity of any liquid chemical we are using.
- 2) **Evaluate the Data** means:
 - a) asking ourselves if we got the results we wanted to get and, if not,
 - b) determining what changes we need to make to reach our target FAC, monochloramine, or FAA level.
- 3) **Make Needed Adjustments** is pretty self explanatory but it's important to realize that the loop does not end with the adjustment. We must collect more data to verify that:
 - a) we actually made the precise adjustment that we intended to make and
 - b) the adjustment produced the outcome we wanted to produce.

As we can see, the basic questions we need to ask ourselves are:

- ◆ What do we need to measure to control the chloramination process?
- ◆ Where is the best spot to test for it?
- ◆ What results are we looking for?
- ◆ What do we do when we don't get it?

COLLECTING THE DATA

In order assure that we collect the data we need (and to avoid collecting unnecessary data), we need to identify our important monitoring sites, the type of data we need to collect at each site, and our target results. (Yeah, this does sound an awful lot like data we need to include in our Monitoring Plan.)

Some of the data we need (like the molecular weight, formula, concentration, and specific gravity of the chemicals we are using) must be obtained from our chemical supplier and other sources. However, most of the data (like target and current residual levels, current feed and flow rates, etc) we have to determine ourselves. For example, we may need to set our target residual at one of our injection points based on the disinfectant residual we need maintain at the end of that disinfection zone but set the target residual at another point based on the residual we want leaving the plant (which, in turn, might be based on the residual we want to maintain in the distribution system).

What do we need to measure?

By now, we should realize that we need to be able to test for at least four different things:

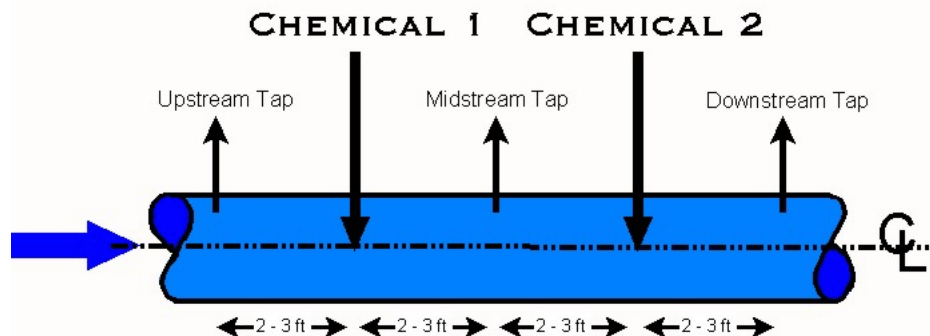
- 1) free chlorine . . . to find out:
 - a) if we added the right amount of chlorine to get the monochloramine residual we want and
 - b) exactly how much ammonia we need to apply.
- 2) free ammonia . . . to find out:
 - a) if we applied too much ammonia or
 - b) exactly how much chlorine we should apply to reduce the ammonia level
- 3) monochloramine . . . our target disinfectant, to find out:
 - a) if we added the right amount of chlorine and ammonia.
- 4) total chlorine . . . to find out:
 - a) if we made any di- or trichloramine and
 - b) how much difference we should expect between our monochloramine and total chlorine results.

However, it is also pretty helpful if we can also be able to determine our chemical/reactant feed rate and water flow rate at each of our injection points.

Where should we test for it?

Obviously, we have to monitor at each sampling point that is required by regulations. For example, we have to monitor at the end of each disinfection zone, at the entry point to the distribution system, and at designated sites in the distribution system. However, we also need to collect process control samples in addition to the regulatory samples. Process control samples are particularly important because they can detect problems before they reach the regulatory sampling point. In general, process control sampling points will depend on where we are adding each chemical but it is always helpful if we have:

- 1) an upstream tap so that we can determine much chemical we need to add before we add it, and
- 2) a downstream tap so that we can determine if we added the right amount of chemical after we added it.



Regardless of which chemical (chlorine or ammonia) we inject first, we should try to separate the injection points by several feet or at least ensure that the injection stingers are placed at about the same depth in the pipe. This arrangement helps us get as much chemical dispersion and mixing as we can when adding each chemical. As the figure indicates, it is usually helpful to have a sample tap upstream of each pair of (chlorine and LAS) injection points, one between the two points, and one after the two points. If we don't have enough room to put the midstream tap, we may be able to run the "midstream tests" by temporarily turning off Chemical 2 and making our measurement at the downstream tap.

We need to remember that competing chlorine reactions can occur very quickly. Consequently, it may not be possible to get an accurate free chlorine reading if chlorine is being applied first and ammonia is being injected only a few feet later. This is because the amount of time it takes to collect and analyze the sample will be much longer than the 10 – 15 seconds it takes for the chlorinated water to reach the ammonia injection point. Since the competing reactions continue to occur during collection and analysis,

the free chlorine residual detected in the sample could be much lower than the residual that actually exists at the time that the ammonia is injected.

On the other hand, if it takes 4 or 5 minutes for the chlorinated water to reach the ammonia injection point, we may be able to get a reasonably accurate reading if we collect the sample quickly and run the test at the sampling site. This is because the very rapid reactions occur within the first couple of minutes of chlorine exposure; after a few minutes of chlorine exposure, the minute or so that it takes to collect and test the sample has less of an impact on the results. If there is 10 – 15 minutes of free chlorine contact time between the chlorine and ammonia injection points, the free chlorine residual in the water will have stabilized enough for sampling and analysis time to have a minimal impact.

What are our targets?

As we just noted, our performance targets for the monitoring sites at each application point are usually based on a performance goal somewhere else in the plant or in the distribution system. These goals tend to vary on a system-by-system basis and even on a seasonal basis within a single system. However, there are some rules of thumb that we can use.

- 1) We need to set performance targets for free chlorine, total chlorine, and monochloramine residuals at each application point.
 - a) The targets within the plant should usually be based on our CT requirements. Therefore, we need to develop a correlation between the disinfectant residuals at the end of each zone and the levels we need to achieve at the application point.
 - b) The targets at the high-service pump station should usually be based on the disinfectant levels that we want to maintain in the far reaches of the distribution system or at our next rechlorination point. Again, we need to understand the relationships that exist between the sample sites. However, we also need to realize that it is going to be much more difficult to use the results at a distant point to control the process because the distribution residuals are influenced by a lot more than just the residual leaving the plant.
- 3) Although we may also need to set a free ammonia target for each application point, the one we set at the entry point to the distribution system is the most important. Free ammonia is a nutrient source for certain bacteria. In addition, free ammonia levels in distribution tend to be significantly higher than those at the plant because monochloramine decays in the distribution system and this decay can release ammonia back into the water. Consequently, we need to keep the ammonia level as low as possible in the water leaving the plant. The target free ammonia level at the high-service pump station should be no greater than 0.05 – 0.10 mg/L.
- 4) Our performance targets need to include:
 - a) an acceptable range . . . what results will we allow before we are willing to make a change in the treatment process
 - b) critical levels . . . what reading(s) would prompt us to make a change and what adjustments would we make if we reached that unacceptable level of performance.

EVALUATING THE DATA

This step in the process control loop is where we compare our test results to our performance targets, determine if we are over-feeding or under-feeding one or more reactants, and then decide what adjustments (if any) we need to make.

WHAT TO LOOK FOR

If Chlorine is Added Before Ammonia

- $FAC = \text{Target } NH_2Cl$

If Ammonia is Added Before Chlorine

- $FAA = \text{Target } NH_2Cl \div \text{Target } Cl_2:NH_3 \text{ ratio}$

After Adding the Chlorine and Ammonia

- NH_2Cl level is within our acceptable range
- Minimal change in the combined chlorine levels, i.e., is $TAC - FAC = TAC - NH_2Cl$?
- FAA as $NH_3 < 0.2 \text{ mg/L}$ within the plant
- FAA as $NH_3 < 0.1 \text{ mg/L}$ at the entry point to the distribution system

WHAT TO DO WHERE TO START

- If NH_2Cl is too high, then
 - Reduce the NH_3 dose &
 - Reduce the Cl_2 dose
- If NH_3 is too high, either
 - Reduce the NH_3 dose or
 - Increase the Cl_2 dose
- If combined chlorine increased, either
 - Increase the NH_3 dose or
 - Reduce the Cl_2 dose

IT'S A BALANCING ACT BASED ON WHERE
WE'RE AT ON THE BREAKPOINT CURVE

BACK TO SCENARIO 2: AMMONIA IS ADDED BEFORE CHLORINE

Let's finish evaluating our second scenario (which we were discussing way back on page 12).

Remember that at this application point:

- 1) we are adding ammonia before chlorine because the water has already gone through breakpoint chlorination;
- 2) we want to achieve a monochloramine residual of about 2.3 mg/L or so;
- 3) current operations produced the following data:
 $TAC = 2.3 \text{ mg/L}$ $FAC = 0.0 \text{ mg/L}$ $Mono = 1.6 \text{ mg/L}$ $FAA = 0.2 \text{ mg/L as } NH_3$;
and
- 4) we needed to answer these two questions:
 - a) Is there already enough ammonia present to get us to our target monochloramine residual of 2.3 mg/L if we just add chlorine or do we need to add more?
 - b) Once we have the right amount of ammonia, how much chlorine do we need to add to reach our target monochloramine residual?

To answer these questions, we need to remember that 1.0 mg/L of chlorine (as Cl_2) will produce 1.0 mg/L of monochloramine (as Cl_2) if we have enough ammonia present. Therefore, we will need to add about 0.7 mg/L of chlorine raise our monochloramine level from 1.6 mg/L to 2.3 mg/L.

We also need to remember that the chemical monochloramine reaction involves one chlorine molecule and one ammonia molecule. Since chlorine molecules have a molecular weight of 71 and ammonia molecules have a molecular weight of 17, the chlorine:ammonia ratio (by weight) is 71:17, or 4.2:1.

To find out if we have enough ammonia present, we divide the amount of chlorine we need to add by our chlorine:ammonia ratio. As the equation indicates, we'll need about 0.17 mg/L of free ammonia (as NH_3) to react with the chlorine we add if there are no competing reactions.

Therefore, if there are no competing reactions, we will need to add 0.7 mg/L of chlorine and no ammonia to reach our 2.3 mg/L monochloramine target. After we add the chlorine, we expect to get the following results:

TAC = 3.0 mg/L FAC = 0.0 mg/L Mono = 2.3 mg/L FAA = 0.03 mg/L as NH₃

because:

- 1) adding the chlorine should also raise our total chlorine residual by 0.7 mg/L (since the total chlorine test kit will detect monochloramine),
- 2) the combined chlorine level will remain 0.7 mg/L (since we didn't form any dichloramine or trichloramine), and
- 3) consuming 0.17 mg/L of our FAA should leave us with an FAA level of about 0.03 mg/L (which we may not be able to see since it is near the lower detection limit of our test kit)

All of these parameters (monochloramine residual, change in combined chlorine levels, and free ammonia level) fall within our desired parameters. Now we have our starting point for making feed rate adjustments.

MAKING THE ADJUSTMENTS

TCEQ has created a pair of spreadsheets to help us set our chemical feed rates. One spreadsheet was designed for plants that feed liquid ammonium sulfate and the other one was designed for plants that feed anhydrous ammonia. Each of the spreadsheets contain three pairs of worksheets; one pair for plants that feed gas chlorine (one for gas chlorine first and one for gas chlorine second), one pair for plants that feed bleach (bleach first, bleach second), and one pair for plants that feed calcium hypochlorite (hypochlorite first, hypochlorite second). After we enter data about our current operating conditions for each injection point into the proper worksheet, the spreadsheet will tell us what adjustments we will probably need to make to our chemical feed rates at each injection point.

However, many operators prefer to use a step-by-step method to calculate their target chlorine and ammonia feed rates rather than using a computer and spreadsheet. The step-by-step calculation uses the same conversion factors as the “mash it all together in a single step” approach used by the spreadsheets. Consequently, both approaches will give the same results.

When using the step-by-step approach, we use the following 11 steps:

- Step 1: Decide what monochloramine residual and free ammonia level we want to have in the water after we add the chlorine and ammonia.
- Step 2: Run total chlorine, free chlorine, monochloramine, and free available ammonia and determine if we need to make any adjustments.
 - A) If we are at our targets, repeat step 2 periodically.
 - B) If adjustments are needed, proceed to step 3.
- Step 3: Figure out how many million pounds of water we would produce during 24 hours if we ran continuously at our current flow rate.
- Step 4: If we are currently feeding chlorine and ammonia at this application point, measure our current feed rates, calculate the current chlorine and ammonia doses, and determine our current Cl₂:NH₃ ratio.

- Step 5: Figure out how much we need to raise the monochloramine residual (in mg/L) to reach our target so that we know what our effective chlorine dose needs to be.
- Step 6: Figure out how much chlorine demand we have in the water so that we can determine what our actual chlorine dose needs to be.
- Step 7: Figure out what our chlorine feed rate should be based on the type of chemical we are using and its concentration (and if we're feeding bleach, its specific gravity).
- Step 8: Decide what our target $\text{Cl}_2:\text{NH}_3$ ratio should be.
- Step 9: Figure out what our ammonia dose (as mg/L of NH_3) needs to be to achieve our target ratio or our desired free ammonia concentration.
- Step 10: Figure out what our ammonia feed rate should be based on the type of chemical we are using and its concentration (and if we're feeding a liquid, its specific gravity).
- Step 11: Go back to Step 1.

Step 1: Set Our Targets

Let's say that we want to have a monochloramine residual of 2.2 mg/L but are willing to accept a reading of 2.0 – 2.5 mg/L (as Cl_2). We also want to maintain a free ammonia level of 0.05 – 0.07 mg/L as NH_3 to minimize dichloramine and trichloramine formation.

Step 2: Run Our Tests

We collect a sample at the tap upstream of our chlorine and ammonia injection point and find:

TAC = 1.9 mg/L FAC = 0.1 mg/L Mono = 1.0 mg/L FAA = 0.05 mg/L as NH_3

We also collect a sample at the tap downstream of our chlorine and ammonia injection point and find:

TAC = 3.0 mg/L FAC = 0.1 mg/L Mono = 1.6 mg/L FAA = 0.0 mg/L as NH_3

Based on our results, we should not assume that we really have free chlorine in either sample because the monochloramine levels are high enough to interfere with the free chlorine test and because monochloramine and free ammonia cannot coexist with free chlorine for very long. However, we also cannot assume that the free chlorine residual in the downstream sample is really 0.0 mg/L because we have no free ammonia present. If FAA is really 0.0 mg/L, then we may have run out of ammonia before all of the chlorine reacted.

Furthermore, the difference between the total chlorine and monochloramine levels increased after we added our chlorine and ammonia. As a result, we should be worried that we may be adding too much chlorine (or not enough ammonia) and forming a little dichloramine. We should also assume that we probably have not formed any trichloramine because our monochloramine level is still pretty high.

Based on these test results, we realize that we need to adjust either (or maybe even both) our chlorine and ammonia feed rates so that we can achieve our target monochloramine residual and free ammonia level.

Step 3: Calculate Our Flow Rate

Our current flow rate at this injection point is 830 gpm. This flow rate is equivalent to 1.195 MGD, or about 10 million pounds per day.

Step 4: Measure Feed Rates and Calculate Doses and Ratio

At this application point, we are currently feeding 6.0 ml/min of LAS followed by 15 ppd of gas chlorine at few feet downstream. The specification sheet on our LAS says that the product contains 38% ammonium sulfate (^w/_w) and a specific gravity of 1.23. Therefore, we are applying 2.3 ppd of ammonia and 15 ppd of chlorine.

Using our feed rate and flow rate information, we can determine that our current chlorine and ammonia dosages are about 1.5 ppm and 0.23 ppm, respectively.

Because we are applying ammonia upstream of chlorine at this application point, we should probably base our Cl₂:NH₃ ratio on our chlorine and ammonia feed rates (since we should assume that most of the chlorine demand results from the ammonia we have put in the water). Based on this assumption, our (applied) Cl₂:NH₃ ratio is 6.5:1.

Remember (from Step 2) we were worried that we might be adding too much chlorine or not enough ammonia because the difference between the total chlorine and monochloramine levels increased after we added our chemicals. Since higher ratios (more chlorine and less ammonia) favors the formation of dichloramine, we should not be too surprised to find that we are operating at a ratio that is higher than the theoretical ratio of 4.2:1.

Step 5: Calculate Desired Monochloramine Dose

To reach our monochloramine target of 2.2 mg/L, we'll need to increase the monochloramine residual by 1.2 mg/L at this application point. This means that we need to apply an effective chlorine dose of 1.2 mg/L (since 1 mg/L of chlorine will produce 1 mg/L of monochloramine if there are no competing reactions). However, since we are willing to accept any monochloramine residual that falls between 2.0 and 2.5 mg/L, our effective chlorine dose can be as low as 1.0 or as high 1.5 mg/L.

Step 6: Determine Chlorine Demand

Because we are applying ammonia upstream of chlorine at this application point, we should assume that most of the chlorine demand results from the ammonia we have put in the water. Still, there might be a little naturally-occurring chlorine demand left after our earlier processes. In addition, we have a relatively high monochloramine target and a relatively low free ammonia target. As a result, we are probably not going to be able to completely eliminate the formation of dichloramine and, therefore, we have a little chlorine demand.

Let's assume that we're going to lose about 0.1 mg/L of the chlorine we add to a competing reaction. If the demand is much higher than we estimated, we'll get more free ammonia than we expect after we make our change. If the demand is far lower than we expected, we'll continue to see elevated combined chlorine levels and no free ammonia.

In Step 4, we determined that we were adding 1.5 ppm (mg/L) of chlorine. Therefore, based on estimated chlorine demand, our effective chlorine dose will be about 1.4 mg/L. Although this effective dose is within the acceptable range we identified in Step 5, let's assume that we decide to lower it to 1.2 ppm so that we can reach our chloramine target of 2.2 mg/L exactly. Based on our estimated chlorine demand, an effective dose of 1.2 mg/L is equivalent to an applied dose of 1.3 mg/L.

Step 7: Determine Desired Chlorine Feed Rate

Based on our flow rate and our 1.3 ppm (applied) dose, we calculate that our gas chlorine feed rate needs to be about 13 ppd instead of 15 ppm.

Step 8: Set our target Cl₂:NH₃ ratio

Because our results were so far from our targets, we should probably select a Cl₂:NH₃ ratio that is pretty close to the theoretical value of 4.2:1. If we had been more on target, we might have selected a ratio that is closer to where we were currently operating (i.e., 6.5:1) than to theoretical. If we want to make sure that we minimize dichloramine formation, we may even decide to try a ratio that is closer to 4:1 or even 3.5:1.

Step 9: Determine our Ammonia Dose (as mg/L of NH₃)

Since we are applying ammonia upstream of chlorine at this injection point, we'll need to base our target Cl₂:NH₃ ratio of 4.2:1 on the chlorine and ammonia dosages that we are applying rather than the measured residuals. We would also need to do this if we were injecting chlorine only a few feet upstream of the ammonia. However, if we had several minutes of free chlorine contact time upstream of our injection point, we would want to base our ammonia dose on the chlorine residual at the ammonia injection point so that we could account for the actual chlorine demand of the water.

Since our free ammonia level upstream of this application point is right where we want it to be, we will need to add enough ammonia to maintain this level after the chlorine has been added. Therefore, based on our target ratio, our ammonia feed rate needs to be 3.1 pounds per day.

If our free ammonia level at the upstream tap was higher than our target, we would want to lower our ammonia feed rate enough to allow the chlorine to consume some of the extra ammonia that is already present at our ammonia application point. Similarly, if the ammonia level at the upstream tap was below our target range, we would have to increase the ammonia dose slightly so that we could reach our target after applying the chlorine.

Step 10: Calculate our Desired Ammonia Feed Rate

In step 4, we calculated that 1 gallon of our LAS solution contains 1.0 lbs of ammonia (as NH_3). Since we need to add 3.1 ppd of NH_3 , we need to set our feed pump so that it feeds 3.1 gpd of LAS, or 8.1 mL/min.

Step 11: Go back to Step 1 and Begin Again

This time through we get the following:

Step 1:

No change in our goals

Step 2:

This time we find the following in the sample we collect from the upstream tap:

TAC = 1.9 mg/L FAC = 0.1 mg/L Mono = 1.0 mg/L FAA = 0.05 mg/L as NH_3

The sample we collect at the tap downstream of our chlorine and ammonia injection point shows:

TAC = 2.9 mg/L FAC = 0.1 mg/L Mono = 2.1 mg/L FAA = 0.06 mg/L as NH_3

Based on the sample results, we should realize that we got pretty close to optimizing the feed rates and $\text{Cl}_2:\text{NH}_3$ ratio at this application point. The combined chlorine residual remained fairly constant at about 0.8 – 0.9 mg/L. The monochloramine level is now within our target zone and we were able to maintain a FAA residual after adding chlorine.

If we decide to make additional changes, we would need to increase the dose of both chlorine and ammonia feed so that we would maintain our 4.2:1 ratio.

Now we just keep repeating step 2

CHAPTER 5:

DISTRIBUTION SYSTEM ISSUES

Nitrification Control

- At the treatment plant
 - Increasing chloramine dose or residual
 - Using chlorine-to-ammonia application ratios closer to 5 mg Cl_2 :1 mg $\text{NH}_3\text{-N}$
 - Removing chloramine-demanding substances like natural organic matter
 - pH control
 - Chlorite addition

Nitrification Control

- In the distribution system
 - Decreasing distribution system residence times
 - Periodic changes to free chlorine
 - Flushing programs
 - Booster stations designed to increase chloramine residual and decrease free ammonia concentration

Biocide-to-Food Ratio

- Biocide: Food Ratio = $\frac{\text{Total Chlorine Concentration}}{\text{Free Ammonia Concentration}}$
- Nitrification observed in tanks where
Biocide: Food Ratio = 0.3 to 1.4 mg Cl₂/mg N
- Nitrification not observed in tanks where
Biocide: Food Ratio = 2 to 5 mg Cl₂/mg N